W.

SERENDIPITY IS NO ACCIDENT

All the inventions that the world contains,
Were not by reason first found out, nor brains;
But pass for theirs who had the luck to light
Upon them by mistake or oversight.
—Samuel Butler

In the celebration or appreciation of human creativity, particularly in science or the practical arts, an uncomfortable puzzle is presented by the role of accident and chance. It is easy to sing the praises of ingenuity or perseverance; cleverness will always have its champions; sheer talent or great breadth and vision will evoke admiration. But the moment we acknowledge the role of chance—of luck—we seem to diminish the creative act and the particular humanity that we attach to it.

Nonetheless, accidental discovery or invention is a common and widely acknowledged fact in modern science and technology. That this should be so is, at first glance, a bit surprising, given the scale and scope of systematic research. How indeed, one might ask, can such unpredictable and uncontrollable events be key elements in a system of science that commands budgets, laboratory, personnel, and national and international organization of such extraordinary size that it is one of the most distinctive products of the twentieth century? And yet it is clear they are, as revealed by just a glance at some of the most widely noted contributions recognized by recent Nobel Prizes in the sciences. A closer look at the "accidental" nature of one of these—the discovery of the form of carbon known as "fullerenes," recognized by the Nobel Prize in Chemistry in 1996—will illustrate just what an interesting role serendipity plays in modern science.

There are philosophers of science who suggest, in fact, that serendipity is fundamental to all science, especially the most creative and important. Thomas Kuhn, in his famous model of scientific revolutions, spoke of the importance of "anomalies" for upsetting the routine of "normal science." As unexpected and unpredicted observations or experimental results, these anomalies may be seen as accidental artifacts of the scientific enterprise, and, yet, crucial to the longer term progress of that enterprise. Other philosophers have likened accidental or unpredictable discoveries to mutations in the genome of a species, and have pointed out that such mutations are indispensable to evolution, and thus to any significant change. There does indeed seem to be a basic level at which the unpredictable, if not the truly accidental, must be an indispensable element of our view of the logic of scientific discovery. To discover something is to uncover that which is not in view. Things that are predictable are arguably not discoveries, although in science we may indeed speak of the "discovery" of the W particle or some such, when a predicted entity is finally brought into view.

Serendipity, as it is more customarily thought of however, is not the stuff of ordinary scientific activity but rather goes outside the boundaries in some sense. The very word is meant to convey being out of control. In a letter to an English agent in Venice in 1754, the English essayist and prolific correspondent Horace Walpole wrote of finding information about some coats of arms. What was interesting was not what he found, but how: "This discovery," Walpole wrote, "indeed is almost of that kind which I call *serendipity*, a very expressive word, which as I have nothing better to tell you, I shall endeavor to explain to you: you will understand it better by the derivation than by the definition. I once read a silly fairy tale, called *The Three Princes of Serendip*: As their highnesses travelled, they were always making discoveries, by accidents and sagacity, of things which they were not in quest of. . . ."²

Rather remarkably, from this beginning, the word *serendipity* made its way into the English language, and by the late nineteenth century had become a common way to refer to accidental discoveries. What Walpole was referring to, however—the tale of the Princes of Serendip—does not actually describe what we would typically think of as accidental discoveries, but rather the insightful use of deduction—the sort of thing that any reader of the detective stories of Arthur Conan Doyle

would recognize in the phrase of Sherlock Holmes, "It's elementary, my dear Watson." The fairy tale that Walpole remembered actually consisted of a series of stories, first published in 1557, about three young princes who had been sent away by their father so they would learn more about the world. The particular adventure that Walpole was recalling was one of the first of the princes' encounters. On the road they met a camel driver looking for his lost camel. While they had not actually seen the camel, they had seen enough to give them the idea of playing a joke on the camel driver. They told him the camel had been spotted nearby, and they supported their claim by the following dialogue:

"Tell me, brother, was the camel you lost blind in one eye?"

"Yes," answered the man.

Then the second brother asked him if, in addition to his blindness, the camel had not a tooth missing.

"Yes," answered the man

Then the third brother asked him if perchance the camel was not lame.

"Yes," answered the man

"Certainly then we met him recently on our way," cried out the three brothers, "and it is quite some time ago that we left him behind."

The camel driver hunted all about in the direction the brothers indicated, but to no avail. He encountered them a day or so later, with great anger—accusing them of probably stealing and selling his camel. The brothers, alarmed at the charge, hastened to explain how they knew so much about the camel, without having actually seen it:

One brother observed that the grass on only one side of the road had been eaten, in spite of the fact that the grass on the other side was much better. The second had noticed cuds of chewed grass that could only have come out of the camel's mouth through a gap in the teeth, and the third had seen that the tracks had shown a pattern of three prints and a dragged fourth foot. These were rather simple deductions, and the princes displayed even more subtle ones in further describing the camel they had never seen. The important point, however, is that they were using what Walpole had described as "accident and sagacity" in piecing together facts. Serendipity, in this sense, however, does not simply refer to "happy accidents." Insight is every bit as important as the accident. Simply to stumble upon something of value is not serendipity; that requires a mental capacity that goes beyond the obvious.

In science there are at least three distinctive forms of serendipity.

These may be relatively pure types, or incidents may in fact share qualities that make strict categorizing difficult. The types may be characterized with names that suggest their most significant historical associations: Columbian, Archimedean, and Galilean.

Columbian serendipity is the most straightforward. When one is looking for one thing, but finds another thing of value, and recognizes that value, we have an obvious example of serendipitous discovery. Of course, even Columbus's own case is a bit fuzzier than we might wish, for he mightily resisted understanding just what it was he had "discovered." In his own mind, he thought that he had found just what he had been looking for, a better route to the Indies. But the result—the European knowledge of the New World—is still intimately associated with his efforts. Accidental discovery or invention is frequently of this sort, although not as universally as might be imagined. When, in 1938, to take a technological example, DuPont chemist Roy Plunkett embarked on experiments to manufacture a new refrigerant, tetrafluorochloroethane (as an alternative to Freon), he accidentally produced a quantity of a whitish waxy solid that turned out to be polymerized tetrafluoroethylene. Plunkett saw that the material had some interesting properties, and the DuPont labs were well equipped to explore these further, and thus was born the material we know as Teflon.

Archimedean serendipity is just as important to science and technology, although it is often less readily recognized. It will be recalled that when Archimedes settled himself into his bath and saw the water displaced by his body and concluded that the quantity of water was proportional to his volume, he had been pondering just how he might accurately measure the volume of an irregular solid (a crown). He did not take a bath with solving that problem as his immediate goal, but the solution—accidentally derived—was evident to him nonetheless and was indeed much sought after. When Charles Goodyear, in 1839, dropped a quantity of molten rubber mixed with sulfur on a hot stove, he marveled at the result—not the charred piece of ruined rubber he would have expected but instead a piece of solid, still workable material that withstood the action of further heating and remained pliable even when cooled. This was, in fact, something he had been seeking for almost ten years, although the act of discovery was itself "accidental." Alexander Fleming, in observing how his culture of staphylococci showed evidence of bactericidal

action around a mold that had accidentally fallen on the petri dish, was seeing something he was particularly eager to see. He had, after all, nine years earlier observed similar action by his own mucous and had isolated lysozyme, a bactericidal enzyme. Seeing the action of the mold that would lead to penicillin was the fulfillment of a long-desired goal. This is not simply a matter of "prepared minds," but of actually finding sought-for results, although by routes not logically deduced but luckily observed.⁴

Galilean serendipity is less widely recognized as "accidental," but it seems impossible to fully comprehend the role of serendipity in science and technology without including it. When Galileo pointed the optics of a good spyglass towards the heavens, it is not clear what he expected to see. But what he saw was far beyond anything he could have imagined. The shadows of mountains on the moon, the moon-like phases of Venus, the "Medician stars" that he in time deduced were moons around Jupiter—all were unexpected marvels, not exactly accidents, perhaps, but nonetheless the discovery of things unsought for and recognized by Galileo's "sagacity." Time and again in science we see this facility for using new instruments or capabilities to generate surprises. We can also readily recognize in these cases that the creative achievement lies not so much in creating the surprise but in seeing what it "means." Making the surprise happen is not, in fact, a trivial accomplishment; we honor Galileo for simply making that telescope and having the wit to think of what he might do with it. But the true contribution to science, as recognized by Nobel Prizes or inclusion in the pantheon of scientific heroes, is in making the surprise fit some larger scheme of meaning.

When Harold Kroto of the University of Sussex received his shared Nobel Prize in Chemistry in 1996, he readily acknowledged the serendipity behind his and his colleagues' achievement, and, indeed, the discovery of the fullerene form of carbon has been cited as an archetypal example of the continuing importance of serendipity in modern science. A closer look at this episode, however, can serve to shed light on just what this means in a world of highly organized and expensive scientific endeavor.⁵

Kroto is a chemist with a long-standing interest in "astrochemistry," the esoteric field that emerged in the late 1960s to study interstellar molecules. He was, in other words, interested in "What's out there?"—what kind of matter fills the space between the stars? The

technique that he and other investigators of this question began to use with great success is called microwave spectroscopy. This uses the phenomenon that every form of matter is associated with a "fingerprint" of microwave radiation, its spectrum, that is distinctive to a particular combination and configuration of atoms. A few years after physicist Charles Townes shared a Nobel Prize in 1964 for the invention of the maser, the microwave precursor of the laser, he led a team of investigators in using new microwave detection and analysis techniques in radio astronomy. New techniques and instruments for the first time made it possible to detect the spectra of complex molecules, and in late 1968 the spectrum of ammonia in interstellar space was found. Over the next decade, dozens of molecules were detected, and the surprising new field of astrochemistry was born.

This was the field that engaged Harry Kroto, and by the 1980s he had established a reputation as a dogged explorer of space molecules, with a particular passion for finding the largest chains of carbon he could. He became convinced that such long, unbranched chains held the key to explaining the so-called "diffuse interstellar bands"—the portions of the interstellar spectrum that some kind of matter, still unknown, absorbs and prevents from making its way to earth. To back this hypothesis, however, it was necessary to create in the laboratory the kinds of long carbon chains thought to exist in space, so that their molecular spectra could be accurately measured and then compared with astronomical data. Harry Kroto became one of the world's best makers of long carbon chains (not *hydro*-carbon chains, which are another, and much simpler, matter altogether), extending them ever longer, aspiring to reach up to thirty-three carbon atoms in a row and beyond.

The path from Kroto's quest for long chains of carbon in outer space to buckminsterfullerene and the Nobel Prize ran through Houston, Texas, and the laboratory of Richard Smalley. To be more precise, it ran through a corner of the Rice Institute laboratory filled by a device known as "AP2." This "laser-vaporization supersonic cluster beam" apparatus was made up of a large vacuum pump, several lasers, canisters of various gases, and an array of electronics for controls and measurement. It formed a particularly effective machine for mashing atoms together into molecular clusters, clusters that in most likelihood would not exist in nature. Smalley had built the machine largely to study clusters of highly refractory

materials, especially semiconductors like silicon. A brief glance at the chemist's periodic table will serve to suggest that a machine that can make clusters of silicon could be asked to do the same for carbon, which sits just above silicon at the head of Group 4 of the elements. Indeed, Smalley made much of creating a combination of silicon and carbon—SiC2—which he was able to calculate was not, in fact, a chain, but a triangle of the three atoms. AP2, while a crude looking bunch of pipes, wires, tubes, and glass, was in fact a superbly designed instrument for not only making unusual cluster molecules, but also for analyzing their spectra with a range of techniques. It is small wonder then that Robert Curl, a Rice associate of Smalley and a molecular spectroscopist, should urge Kroto to take a look at the machine once he heard of his British colleague's special enthusiasm for carbon clusters.

This was, at one level, all that was necessary to set the stage for the serendipity that went to work in September 1985 and yielded the fullerenes. Harold Kroto expressed enthusiasm for the possibility of putting AP2 to work in making his longer carbon chains, and Smalley finally agreed to yield some time from his semiconductor experiments, perhaps as a courtesy to Curl. It had been more than a year since Kroto had first eyed AP2 and thought about the possibilities, but he was still enthusiastic, and he made his way to Houston on just a few days' notice. Meanwhile a couple of Smalley's graduate students started testing how AP2 responded to graphite—pure carbon—as a test material. Right away they noticed something peculiar. One portion of AP2, the time-of-flight mass spectrometer, was used to give a quick and simple reading of the relative amounts of molecular clusters of different sizes produced by a particular operation. By giving the clusters an electric charge and then hurling them toward a target, the device measured the time each took to make the trip. This time is proportional to the size of each cluster, and thus the relative numbers of each size can be charted on a "mass spectrum." The spectrum showed that they produced much higher numbers of even-numbered clusters than odd-numbered ones, once the size exceeded thirty or forty atoms. The published literature prepared them for this result, even though they couldn't explain it. But it did not prepare them for the fact that at a sixty-atom cluster (C_{60}), the numbers were so great they went entirely off the scale, and a somewhat smaller and equally inexplicable peak was

visible at C_{70} . It was impossible, however, to determine if this was indeed significant, and so they moved on in their preparations for Kroto's visit. A mere observation, we are again reminded, does not constitute true serendipity.

For the Rice scientists, carbon was just another potential target for their wonderful machine. They were not indifferent to its special behavior or the wide interest it held for many researchers, but it held no special place in the constellation of chemical possibilities. Such was not at all true for Harold Kroto. For him, AP2 was a device to make and study larger earbon clusters, to get closer to the secret of the diffuse interstellar bands —what he called, with a measure of hyperbole, "the last great problem in astronomy." The workers in Houston were not, in fact, the first to put earbon into an AP2-like device; the year before researchers at Exxon Corporation in New Jersey (Eric Rohlfing, Donald Cox, and Andrew Kaldor) had done so, and had actually reported that C₆₀ produced a pronounced peak in the mass spectrum results. The significance, however, was lost on the Exxon researchers. The significance was by no means readily apparent to the Rice experimenters either. They were, after all, engaged in trying out the instrument to see if it could produce the species of carbon chains that Harry Kroto's hypotheses about the interstellar matter required. The size of those chains or clusters was somewhat smaller than C_{60} —more in the range of twenty or thirty earbon atoms, with hydrogen at one end and nitrogen at the other. There was real difficulty, however, in getting AP2 to produce products with the hydrogen and nitrogen ends, and every time that earbon clusters were produced, under a variety of conditions, the C_{60} peak was always there—sometimes growing to fifty times the size of its neighbors (the smaller C_{70} peak was also persistent).

In these circumstances, the phenomenon could no longer be ignored. Furthermore, the conditions under which the C_{60} peak was magnified suggested that this was an unusually stable molecule, not some fleeting artifact of the conditions in the instrument. Indeed, it appeared to share the properties that organic chemists call "aromatic," which characterize molecules that have limited capacity for taking on other atoms in addition and that are often very symmetrical and stable in configuration. Now Kroto, Curl, Smalley, and their assistants began to tackle the question of what this peculiar substance was. What cluster of sixty carbon atoms

could be so sturdy in a reactive environment and yet resist additions? The long chains that Kroto had been experimenting with would not qualify, since they always possessed loose ends that would react readily, and would typically break apart as well. The same was true for carbon arrayed in sheets of attached hexagons—the form that made up graphite; there were always many dangling, reactive carbons and there was no reason why a sixty-atom sheet would be more stable than some other. It was, in other words, largely by process of elimination that the men at Rice came up with their very surprising, very elegant, and very significant solution: C_{60} was probably a closed solid, roughly spherical in form, in which every carbon atom was safely and securely attached to three other carbons, affording little opportunity for adding other atoms, carbon or otherwise, and resisting breakage or splitting.

It took some pondering, and experiments with toothpicks and Gummy Bears, with cut-out polygons, as well as recollections of children's cardboard star charts, and finally of Buckminster Fuller's geodesic domes, to yield the beautiful, symmetrical nearly spherical form of what was soon dubbed, initially (one guesses) tongue in cheek, "buckminsterfullerene." It was a mathematics professor at Rice who informed the researchers, when they asked about the regular polygon, with sixty vertices, twenty hexagons, and twelve pentagons, that it was called a truncated icosahedron, but would be more familiar to most people as an ordinary soccer ball. The pentagons turned out to be the key to the geometry. An array of hexagons will produce a flat sheet, and nothing else, but when some hexagons are turned into pentagons, the sheet will begin to curl on itself. In the right numbers, with the right distribution, the curving will yield a near sphere—the C₆₀ "buckyball." In different numbers, with appropriate distribution of pentagons among the hexagons, the geometry will yield slightly different shapes, the most stable alternative being a slightly elongated polygon with seventy vertices—the C_{70} observed in the experimental spectra. This was one of those moments in science in which the sheer beauty of the discovery was a key element in convincing the originally skeptical researchers that their hypothesis, actually supported by rather slender experimental evidence, just had to be the right one.

To the men in Houston in September 1985 the spherical carbon atom was a complete novelty—a surprise both experimentally and conceptually. But as so often happens in the large and complex arenas of

modern science, there was plenty of anticipation, once one knew what to look for. Not only had an English essayist, David Jones, once speculated about the possibility of "a closed spherical shell of a sheet-polymer like graphite," but in the late sixties and early seventies Japanese and Russian chemists had gone so far as to publish the calculations that showed no theoretical barriers to such a configuration of carbon atoms. In the early 1980s at least a couple of American chemists speculated on the possibility of synthesizing such a molecule, although they never overcame widespread skepticism. But while the carbon-atom soccer ball may have been imagined, anticipated, and theoretically justified, it was hardly less a surprise to the scientific community when it was announced in *Nature* in October 1985 than it had been to Kroto, Smalley, and company. It is one thing to speculate about a structure—organic chemistry, in particular, is filled with marvels of imagination—but it was entirely different to find evidence of it. The novelty did not end there, however. To a degree, it was equally marvelous when, beginning in late 1989, Donald Huffman of the University of Arizona, and Wolfgang Kratschmer at the University of Heidelberg, with their assistants, began announcing the creation of quantities of C_{60} in "laboratory-produced carbon dust," as they put it in one of their early papers. To move fullerenes from the realm of the scarce and exotic into the nature all around us, filled with dust and soot, was to remake a novelty into a hitherto unsuspected but fundamental part of our universe—as big a surprise as anything twentieth-century chemists were to uncover.

The end of surprise would be the end of science. To this extent, the scientist must constantly seek and hope for surprises. But in an activity that is supposed to be fundamentally rational and orderly, this is neither easy nor comfortable. The awkwardness is visible when we look more closely at the sources of surprise in the fullerene story. For Harry Kroto, this was a Columbian episode. He was looking for a way to make long, observable carbon chains, and he instead encountered a unique and beautiful sphere. For Dick Smalley, on the other hand, the experience was Galilean. His wonderful and clever instrument, AP2, was pointed to a new part of the chemical heavens, and it saw new and unexpected things. Indeed, in his published Nobel lecture, Smalley captioned a picture of AP2 as the "apparatus that discovered C_{60} and the fullerenes." It was not "used to discover," but was indeed the discoverer itself. To him, the creation of

an instrument like AP2 made the discovery of the fullerenes inevitable. Bob Curl's account, in yet another contrast, has the air of the Archimedean about it. It is not that any of the researchers were looking for C_{60} , but the conjectures of the molecule's potential existence were in the literature. The experiments of September 1985, while directed to other ends, were to Curl ultimately the tests and confirmations of these conjectures, at least from a kind of impersonal, universal perspective. And so we can now understand that serendipity, more than we might have believed, is truly in the eye of the beholder.

Of course, surprises will not cease, nor will science. The quintessential joy of serendipitous science lies in its capacity to remind us that, as much as we know, we know only a fraction of what is to be known. As the accidents tell us and the sagacity to use them confirms, we do not even truly know what it is we do not know.

Notes

¹Thomas Kuhn, *The Structure of Scientific Revolutions* (Chicago: U of Chicago P, 1962) For the "mutation" analogy, see, for example, Aharon Kantorovich, *Scientific Discovery: Logic and Tinkering* (Albany State U of New York P, 1993), especially chapters 1 and 5

²Horace Walpole to Horace Mann, January 28, 1754, as quoted in James H. Austin, Chase, Chance and Creativity: the Lucky Art of Novelty (New York, Columbia UP, 1978) 69

³See T. Remer, ed., Screndipity and The Three Princes: From the Peregrinaggio, of 1557 (Norman: U of Oklahoma P. 1966)

¹ Prepared minds" alludes to Louis Pasteur's oft-quoted statement that "in observation, chance favors only prepared minds" ("Dans les champs de l'observation, le hæard ne favorise que les espirits préparés.")

The discovery of the fullerenes is covered in numerous accounts. The most useful are two monographs. Jim Baggott, Perfect Symmetry, the Accidental Discovery of Buckminsterfullerene (New York Oxford UP, 1994) and Hugh Aldersey-Williams, The Most Beautiful Molecule: the Discovery of the Buckyball (New York: John Wiley & Sons, 1995). The discussion here also draws on the Nobel lectures. Robert F. Curl, Jr. "Dawn of the Fullerenes: Experiment and Conjecture," Harold W. Kroto, "Symmetry, Space, Stars, and C₆₀," and Richard E. Smalley, "Discovering the Fullerenes," all in Les Prix Nobel, 1996 (Stockholm Almqvist & Wiksell International, 1997)

⁶David Jones (as "Ariadne"), New Scientist. 32 (Nov. 3, 1966): 245; Eiji Osawa, Kagaku, 25 (1970): 854-63; D. A. Boehvar and E. G. Gal'pern, Proceedings of the Academy of Sciences, U.S.S.R., 209 (1973). 610-12, Robert A. Davidson, "Spectral analysis of graphs by cyclic automorphism subgroups," Theoretica Chemia Acta, 58 (1981): 193.

⁷See the three laureate lectures in Les Prix Nobel, 1996 (note 5)